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Synthesis and Characterization of Zinc oxide Nanocrystals from Chemical and Biological methods and its Photocatalytic activities

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Abstract: In this paper we report the synthesis and characterization of Zinc Oxide (ZnO) nano crystals by both chemical (precipitation method) and biological methods. This study also investigates the effect of molarity concentration on structural and surface morphology of ZnO nanocrystals. In simple precipitation method ZnO nanocrystals are synthesized using three different molarity concentrations. In biological method highly stable ZnO nanocrystals are prepared from Aloe vera leaf extract. The crystallinity and surface morphology of synthesized nanocrystals were characterized by X-ray diffraction analysis and Scanning electron microscopy. SEM analysis shows that the synthesized Zinc Oxide nanocrystals are in hexagonal structure. The photocatalytic activities of the synthesized samples are evaluated for Methylene blue (MB) degradation under UV light irradiation.
Key words: ZnO nanocrystals, Precipitation method, biological method, Aloe vera.

1. Introduction

Most of the investigations are focused on Zinc Oxide nanocrystals to photodegrade various organic pollutants under ultra-violet light (λ<365nm) [1,2]. Zinc Oxide a wide band gap (3.37eV) semiconductors, is an important functional material because of its variety of important properties such as sensors, electrical, photovoltaic and photocatalytic properties. Zinc Oxide nanocrystals are given much attention due to the size and morphology dependent properties. Additionally, ZnO has been found highly attractive because of its remarkable application potential in solar cells, piezoelectric devices, UV absorbers, pharmaceutical and cosmetic industries [3-8]. Potentially, ZnO removed all the dyes and water pollutants from textile effluent under UV light have been proved [9-14].

ZnO nanocrystals have been synthesized by various routes, which are classified by physical, biological & chemical methods. Solution based synthetic methods mainly employ a base such as NaOH, NH_4OH, organic amines etc [15-18]. Although different biological based synthetic methods are known for ZnO are sought by researchers. Biological process has led to the development of an eco-friendly approach for the synthesis of nano particles. The use of non-toxic materials like plant extract & bacteria for synthesis of silver nano particles offers numerous benefits of pharmaceutical application [19]. Synthesis of ZnO nano structures using L-lysine, amino acid [20] and lemon juice [21] have been reported by various researchers. Bio-synthesis of gold nano particles by plant alfalfa have been reported by Gardea-Torresdey et al., [22]. Herein, two different methods (chemical and biological) have employed for synthesis of ZnO nano particles in the form of nano rods. To the best of our knowledge, synthesis of ZnO nano rods using Aleo vera and Zinc acetate by precipitation method has never been reported. The effect of reaction condition in chemical synthesis (different molar concentration), photo degradation of methylene blue dye (both chemical & biological methods) and particle size of Zinc Oxide nano rods has also been investigated.

2 Experimental

Zinc Acetate [$Zn(COOCH_3)_2$, sodium hydroxide [NaOH] and methylene blue dye are purchased from Nice chemicals, India. De-ionized water was used throughout this study. The Aqueous solution of $Zn(COOCH_3)_2$ and NaOH were prepared in different molar ratio [0.5M:0.1M , 1M:0.1M , 1M:0.5M]. Aqueous solution of Zinc Acetate solution was stirred for 20 minutes. While at room temperature aqueous NaOH was added drop wise to $Zn(COOCH_3)_2$ solution. The mixed solutions were stirred continuously at 600 rpm for 2 hours. The resulting milk white precipitate from the reaction between $Zn(COOCH_3)_2$ and NaOH solutions were collected by triple centrifugation and washed by de-ionized water respectively. The precipitates collected after washing were dried at 70^{o}C. The synthesized particles are annealed at 400^{o}C for 2 hrs in programmable furnace to grow the ZnO nanocrystals. The typical procedure was employed for different molar concentration of ZnO nano particles.

For biological synthesis, 2 kg of Aloe leaf was harvested from agriculture field in Erode, Tamilnadu. A portion of aloe leaf (500 g) thoroughly washed, finely cut and boiled, using de-ionized water. The resulting extract was stored in air-tight container for further experiments. From remaining portion of aloe leaf (500 g) inner gel broth was crushed by adding enough de-ionized water to make a thin paste. The gel paste was stored in refrigerator for further experiments. A typical procedure was employed for both aloe extract & gel. Later, zinc acetate solution was stirred for 20 min and required amount of aloe extract was added drop by drop. The mixture was continuously stirred at 800 rpm for 3 hrs. The pale-yellow color precipitate from the reaction was centrifuged and washed with de-ionized water. The washing and centrifuging was repeated several times using ethanol and water. The obtained samples were dried at 70^{o}C for 8-9 hrs in hot air atmosphere.

To identify the crystal phase and crystallite sizes of the synthesized nanocrystals X-ray diffraction (XRD) studies were carried out using Shimadzu**,** XRD-6000 diffractometer at room temperature, using CuKα radiation (λ=1.5406Å) with accelerating voltage of 40 kV and the emission current of 30 mA. The morphology of samples was analyzed using scanning electron microscope (JOEL JSM-6390LV). The experimental suspension was prepared by adding 0.05g catalyst into 250 ml methylene blue aqueous with concentration of 10 ppm. The samples are kept in quartz photochemical reactor, 12W ultra violet lamp (Philips) with wavelength peak at 354nm used as a light source. The progress of photocatalytic degradation was carried out by different time interval (1h, 2hrs, 3hrs, 4hrs). The absorption properties of the synthesized samples are characterized by UV-Vis Spectrophotometer (Bigvision 2371) wavelength of 350nm.

3 Results and Discussion

3.1 Biosynthesis and characterization of ZnO Nano flakes

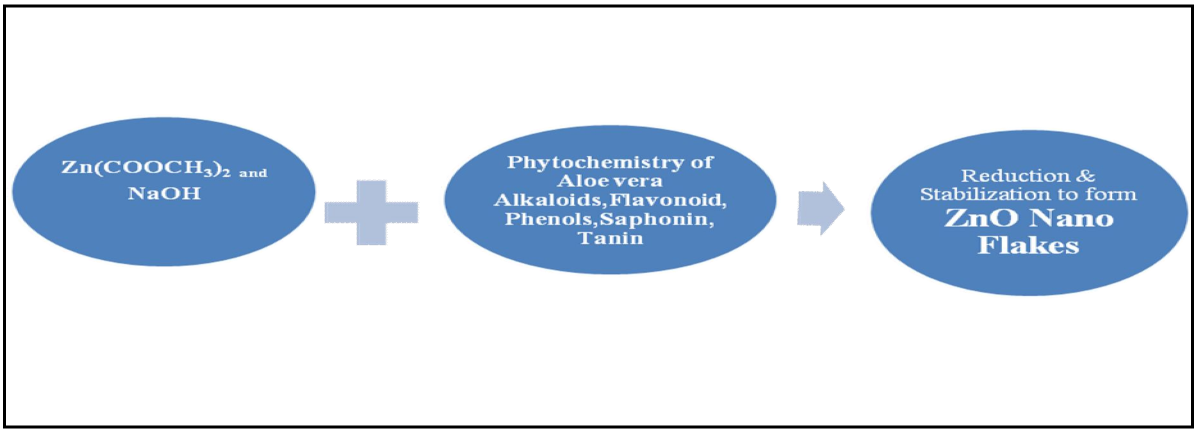


Fig 1: Schematic diagram of formation of AgO Nano fluids

The quantitative analysis of ZnO nanoflakes was carried out based on the visual observation of color formation. Natural product namely Alkaloids, Flavanoids,Phenols, Saphonin,Tanin are main constituents of Aleo vera that act as stabilizing agents[23].It is suggested that these natural products are responsible for reduction of Zinc acetate to Zinc Oxide nano particles. In addition, these molecules also act to stabilize the nanoparticles shown in fig.1.Thus it concluded that Aleo Vera extract act as both reducing and stabilizing agents for the formation of Zinc Oxide nano particles.

3.2 X – ray diffraction analysis

Fig-2(a) shows the X-ray diffraction pattern of the synthesized ZnO nanorods and ZnO nano flakes. The sharp and clear diffraction peaks reveals that the synthesized ZnO nanorods have high quality. All the diffraction peaks in the XRD pattern can be indexed to the hexagonal structure of ZnO with fine crystallinity. The diffraction peaks at 2θ (degree) of 31.76, 34.43, 36.267, 47.569, 56.62, 62.88, 67.98 and 69.12 are respectively indexed to (100), (002), (101), (102), (110), (103), (112) and (201) planes of ZnO. The lattice parameters have been calculated using the relation [24,25]

$1/d^2 = 4/3[(h^2+hk+k^2/a^2)]+l^2/c^2$

The calculated values are a=3.248 Å and c=5.215 Å, the values are in good agreement with the reported standard values a=3.249 Å and c=5.206 Å (JCPDS no. 36-1451). The average particle size (D) are calculated using the Scherer's semi empirical formula $D= k \lambda / \beta \cos\theta$

Where λ is the wavelength of the X-ray (1.5406 Å), k is the shape factor (≈ 0.94), β is the full width at half maximum (FWHM) and θ is the Bragg angle (degree). The value of FWHM was obtained by performing profile fitting using an XRD pattern processing software. The average crystallite size was estimated to be 31 nm.

Fig-2(b) shows that diffraction peaks of ZnO nano flakes the peaks present at 2θ (degree) of 31.95, 34.70, 36.52, 47.78, 57.07, 63.15, 67.72, 68.94 respectively indexed to (100), (002), (101), (102), (110), (103), 112) and (201) planes of ZnO. The calculated lattice parameter values are a=3.267 Å and c=5.243 Å, the values are in good agreement with standard values. The calculated average particle size is 34 nm. The diffraction peaks of ZnO nanorods and nano flakes have the hexagonal wurtzite structure. Nano rods [Fig-1(a)] shows sharp and straight peaks compared with nano flakes [Fig(b)]. At the same time, there is no additional peaks in the pattern, which indicates that all the precursors have been completely decomposed. All the synthesized nanocrystals are in mesophorous state.

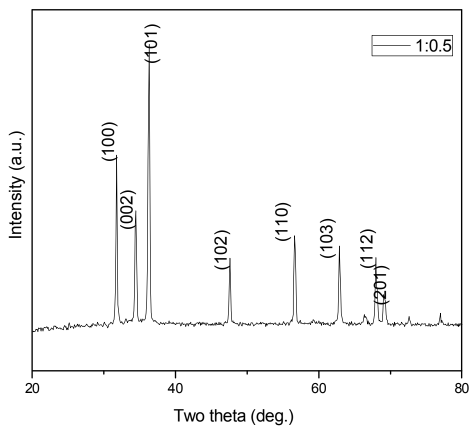


Fig 2(a) XRD-pattern of ZnO nanorods prepared using 1:0.5M

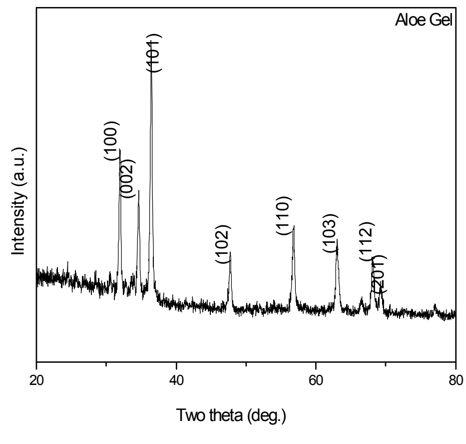
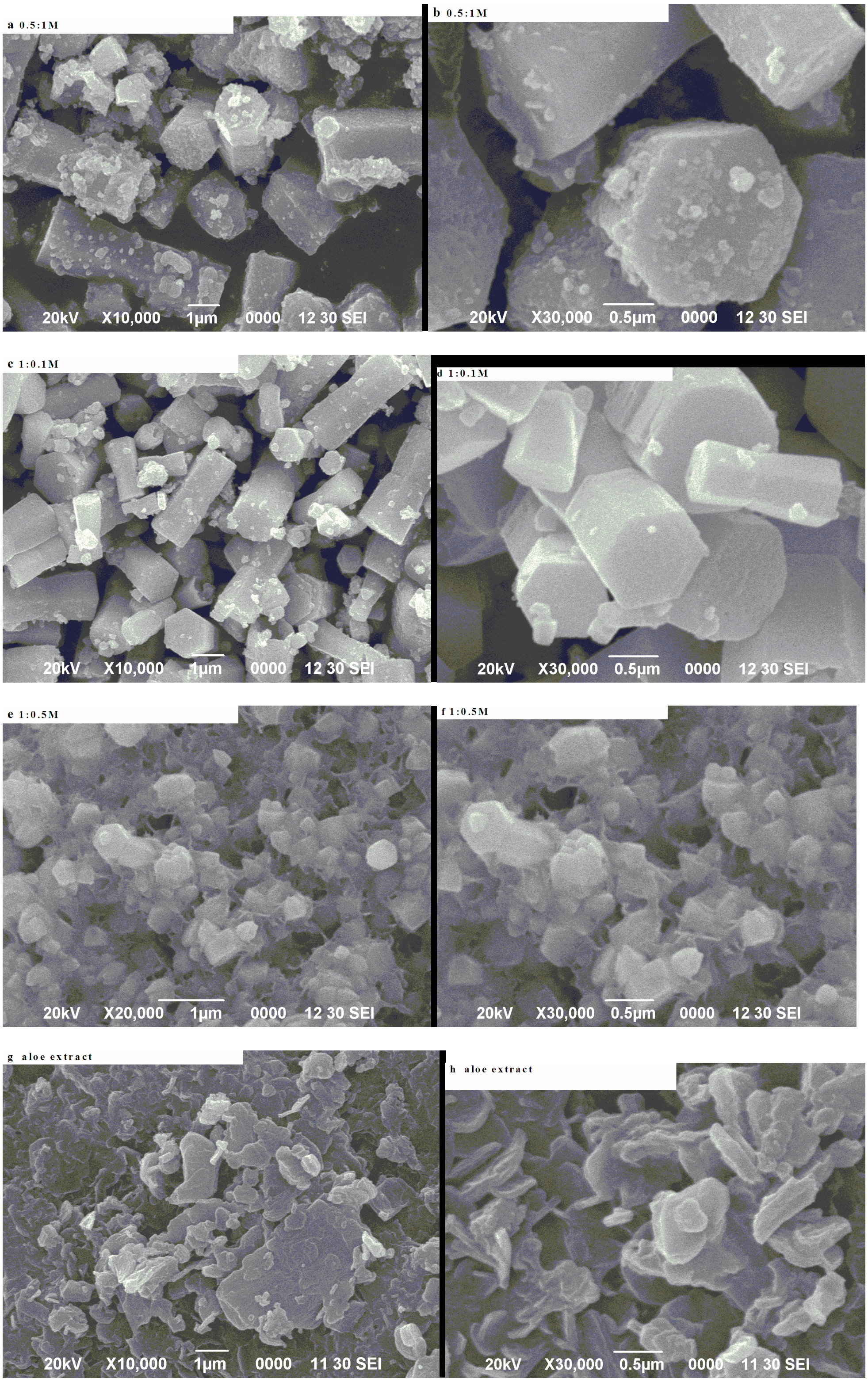


Fig 2(b) XRD-pattern of ZnO nanocrystals prepared using aloe gel

3.3 Scanning Electron Microscope analysis

Figure 2 shows the SEM imagesof the synthesized ZnO nanocrystals using precipitation and biological method. From the figure, it clearly shows that the ZnO nanocrystals synthesized from chemical method possess rod like structures, and agglomerated hexogonal shapes. ZnO nano particles from biological method seems like a nano flakes. Difference of the surface morphology between chemically synthesized ZnO and biologically synthesized ZnO, was obviously observed from the images. The figure also shows that ZnO nanocrystals synthesized from biological method gives irregular bulks than the ZnO nanocrystals synthesized from 1:0.5 molar concentrations. The ZnO nanocrystals synthesized using 0.5:1 M and 1:0.1 M concentration shows agglomerated hexagonal shapes.



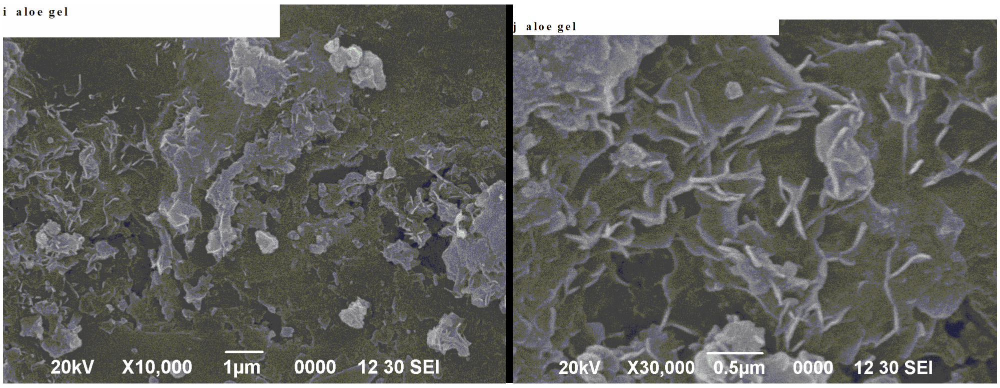


Fig. 3. SEM image of (a,b.c,d,e,f) ZnO nano rods and (g,h,i,j) ZnO nano flakes

3.4 Photocatalytic Applications

The optical absorption in the UV region and corresponding photo efficiency influences the use of ZnO nanorods and nano flakes for photo catalytic activities.The photocatalytic activity of the ZnO nanorods and nano flakes was evaluated by the degradation of 10ppm of MB at natural pH. Fig.4 (a) shows the effect of irradiation time of the catalyst on the absorbance of methelene blue for ZnO nanorods and nano flakes. It can be seen that initial slopes of the curves representing rate of absorbance, it increase greatly by increasing the irradiation time from 1 hour, 2 hrs and 3 hrs and 4 hrs of the catalyst. Figure 4 also indicate the comparison of all the molar concentrations of ZnO nanorods synthesized using chemical method, it clearly infers that the 1:0.1 M concentration achieves higher photocatalytic activity. The figure clearly shows that the ZnO nanocrystals synthesized from chemical method shows higher catalytic activity than the ZnO nanocrystals synthesized from biological method. The reason may be the formation of nanorods during chemical synthesis. The nanorod surface shows higher surface area than the other structure it may the reason for better catalytic activity. Due to this more negative surface charges are produced on the ZnO nanorod surface, these charges readily attract the methylene blue molecule and degrade it. The poor degradation of methylene blue by the nano flakes is due to positive surface charge on the surface. The positive charge on the ZnO surface does not pay attention to attract the methylene blue molecule since it is a cationic dye [26].

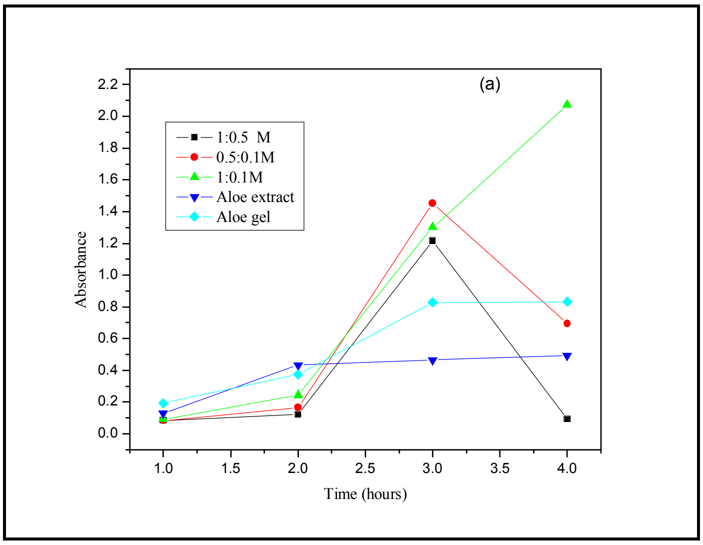


Fig. 4. Photocatalytic activity of ZnO nanorods and nanoflakes as a function of irradiation time.

4 Conclusions

ZnO nanoparticles have been synthesized from both chemical and biological methods respectively. X-ray diffraction analysis reveals that the prepared ZnO nanorods exhibit hexagonal structure. The formation of ZnO nanorods and nano flakes has been confirmed by using SEM image. The Zinc Oxide nanoparticles show distinct poly dispersity and the average particle size of 31 nm. The photo catalytic activity of ZnO nanorods and flakes were carried out on methelene blue dye by varying the irradiation time. ZnO nanorods synthesized using 1:0.1 molar concentration achieves higher photocatalytic activity than the other concentrations and aloe.

5 References

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